Natural Gas Liquefaction

TEP 10 – Gas Processing and LNG – Fall 2008

Jostein Pettersen

Simplified LNG plant block diagram
Hammerfest LNG plant - block flow diagram

**Gas conditioning (pre-treatment)**

- **Acid Gas (CO₂ and H₂S) removal**
  - Acid gas causes corrosion, reduces heating value, and may freeze and create solids in cryogenic process
  - Typical requirements for LNG: Max 50 ppmv CO₂, Max 4 ppmv H₂S (ppmv - parts per million by volume)

- **Dehydration (water removal)**
  - Water will freeze in cryogenic process
  - Typical requirement: Max 1 ppmv (weight) H₂O

- **Mercury removal**
  - Mercury can cause corrosion problems, especially in aluminium heat exchangers
  - Requirement: Max 0.01 μg/Nm³
Gas quality constraints for gas liquefaction

- Typically examining trace components which
  - Freeze
  - Are corrosive
  - Are poisonous

- Other components which may also require to be removed are:
  - N₂ rollover concerns
  - C₂/C₄ – value enhancement

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
<th>Unit Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>&lt; 1 ppmv</td>
<td>Dehydration</td>
</tr>
<tr>
<td>CO₂</td>
<td>&lt; 56 ppmv</td>
<td>Acid Gas Removal</td>
</tr>
<tr>
<td>H₂S</td>
<td>&lt; 4 ppmv</td>
<td>Acid Gas Removal</td>
</tr>
<tr>
<td>Organic S (RSH, CO₂, C₂H₆)</td>
<td>&lt; 56 ppmv</td>
<td>Acid Gas Removal</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt; 10 ng/Nm³</td>
<td>Mercury Removal</td>
</tr>
<tr>
<td>C₂⁺ Hydrocarbons</td>
<td>&lt; 1000 ppmv</td>
<td>Front End of Liquefaction</td>
</tr>
<tr>
<td>Aromatics (BTX)</td>
<td>&lt; 10 ppmv</td>
<td>Front End of Liquefaction</td>
</tr>
</tbody>
</table>

Source: Advantica

Natural gas and LNG composition
Design data for Hammerfest LNG plant

<table>
<thead>
<tr>
<th>Component</th>
<th>Slug catcher mol %</th>
<th>Liquefaction plant mol %</th>
<th>LNG mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>2.51</td>
<td>2.67</td>
<td>1.10</td>
</tr>
<tr>
<td>Methane</td>
<td>80.02</td>
<td>86.34</td>
<td>91.92</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.97</td>
<td>6.54</td>
<td>5.59</td>
</tr>
<tr>
<td>Propane</td>
<td>2.50</td>
<td>2.68</td>
<td>1.11</td>
</tr>
<tr>
<td>Butane</td>
<td>1.22</td>
<td>1.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.58</td>
<td>0.35</td>
<td>0.04</td>
</tr>
<tr>
<td>C₆⁺</td>
<td>1.62</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>Aromatics</td>
<td>0.23</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.20</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.0005</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>0.81</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MEG</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Example of ageing/weathering during LNG transport

Calculated ageing effect during the voyage from Melkøya to USA, Cove Point

Calculated according to ISO 6976 – based on real gas

Nitrogen Removal

Nitrogen need to be removed from LNG in order to meet

* Storage and transport specification (Roll Over)
* Fuel gas requirements
* LNG Heating Value requirements

Systems to handle N₂ will vary in complexity, from simple end flash drums, to complex distillation columns systems for separating N₂ from the LNG
Example of end flash with LNG turbine
Flash gas (containing nitrogen) used as fuel gas

LNG at near-atmospheric pressure pumped to storage tank

Qatargas LNG plant layout
Qatargas

Gas turbines and compressors

CO₂ absorber

MCR Heat Exchanger

CCR

Atlantic LNG – Trinidad (Air cooled)

Jetty

Jetty

Compressors

Air cooled condenser s

Cold boxes (Heat exchangers)
**Gas liquefaction process - ideal**

*Example: Natural gas at 60 bar, 10°C ambient temperature*

- Heat is removed as the gas is cooled at gliding temperature
- Ambient temperature 10°C
- Heat removed during liquefaction ($Q$), and ideal work ($W$), are shown as areas
- Gas pressure has a large influence on work
- Ideal work of liquefaction: Natural gas at 60 bar: 0.11 kWh/kg
  (0.8 % of Lower Heating Value)
Energy (fuel gas) use for liquefaction

- Liquefaction process 2nd law (exergy) efficiency typically around 50%
- Typical fuel use 5-10% of feed
- Ambient temperature and feed gas pressure has large effect

Energy input as % of LHV

Exergy efficiency of liquefaction cycle, %

Efficiency of power generation:
- 30 %
- 60 %
- 100 %

Natural gas cooling

- Cooling of natural gas stream occurs over large temperature span
- Heat must be removed from natural gas stream at varying temperature
- Temperature of evaporating refrigerant must be as high as possible to reduce power need for heat pumping
- Close match between NG temperature curve and refrigerant temperature can be achieved by
  - using many stages of evaporation temperature (cascade process), or
  - using a refrigerant that evaporates at gliding temperature (mixed refrigerant process)
Temperature difference in heat exchangers is increasingly important at lower temperatures

- Sub-ambient temperature
- $\Delta W = $ extra power input needed to compensate for heat transfer across a temperature difference of $\Delta T = 1$ K
- $\Delta W$ grows more than exponentially as temperature level $T$ is reduced

Consequence: $\Delta T$ need to be reduced as much as possible at low temperatures

Natural gas path through liquefaction

**pressure-enthalpy diagram (C1: 89.7%  C2: 5.5%  C3: 1.8%  N2: 2.8%)**

- Subcooling
- Liquefaction
- Precooling
- Expansion
- JT Throttling
- End flash
- LNG

**Ambient temp 10°C**

- Increased work input
- Reduced work output

- Consequence: $\Delta T$ need to be reduced as much as possible at low temperatures

- Natural gas path through liquefaction

- Pressure-enthalpy diagram (C1: 89.7%  C2: 5.5%  C3: 1.8%  N2: 2.8%)
Simple vapour compression refrigeration system – Flow circuit

- Heat sink (Air/water)
- Condenser
- Evaporator
- Condensing refrigerant
- Evaporating refrigerant
- Expansion valve
- Compressor
- Fluid to be cooled

Refrigeration cycle in \( \phi h \)-coordinates (propane)

- Evaporation at \(-30^\circ C\)
- Condensation at \(30^\circ C\)
- \(40^\circ C\) at Compressor discharge

- Evaporating temperature \(-30^\circ C\)
- Condensing temperature \(30^\circ C\)
Refrigeration cycle in \( T_h \)-coordinates (propane)

Refrigeration cycle in \( T_h \)-coordinates (propane)

Vapour pressure of pure fluids relevant for LNG processes
# Data for some relevant fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>NBP °C</th>
<th>dhNBP [kJ/kg]</th>
<th>Triple point °C</th>
<th>Triple point bara</th>
<th>Critical point °C</th>
<th>Critical point bara</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen N₂</td>
<td>-195.75</td>
<td>202,678</td>
<td>-210.0</td>
<td>0.125</td>
<td>-146.95</td>
<td>33,944</td>
</tr>
<tr>
<td>Methane CH₄</td>
<td>-161.45</td>
<td>522,080</td>
<td>-182.5</td>
<td>0.117</td>
<td>-82.55</td>
<td>46,002</td>
</tr>
<tr>
<td>Ethylene C₂H₄</td>
<td>-103.71</td>
<td>487,132</td>
<td>-169.2</td>
<td>0.0012</td>
<td>9.20</td>
<td>50,359</td>
</tr>
<tr>
<td>Carbon dioxide CO₂</td>
<td>-78.45</td>
<td>392,780</td>
<td>-56.6</td>
<td>5.170</td>
<td>31.05</td>
<td>73,765</td>
</tr>
<tr>
<td>Ethane C₂H₆</td>
<td>-88.65</td>
<td>496,999</td>
<td>-182.8</td>
<td>0.000013</td>
<td>32.25</td>
<td>48,839</td>
</tr>
<tr>
<td>Propane C₃H₈</td>
<td>-42.07</td>
<td>431,517</td>
<td>-187.6</td>
<td>1.960E-09</td>
<td>96.67</td>
<td>42,496</td>
</tr>
<tr>
<td>n-Butane C₄H₁₀</td>
<td>-0.45</td>
<td>389,746</td>
<td>-138.3</td>
<td>6.740E-06</td>
<td>152.05</td>
<td>37,997</td>
</tr>
</tbody>
</table>

**Normal boiling point, at 1.013 barₚ**

**Enthalpy of evaporation at NBP**

**Normal sublimation temperature (NBP lower than triple point temp)**

---

**Phase envelope (for a given composition)**

<table>
<thead>
<tr>
<th><strong>Bubble Point Curve</strong></th>
<th>Boundary between liquid phase and 2-phase region</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dew Point Curve</strong></td>
<td>Boundary between gas phase and 2-phase region.</td>
</tr>
<tr>
<td><strong>Critical Point</strong></td>
<td>Location where bubble point and dew-point curves meet.</td>
</tr>
<tr>
<td><strong>Cricondentherm</strong></td>
<td>Highest T in phase envelope.</td>
</tr>
<tr>
<td><strong>Cricondenbar</strong></td>
<td>Highest P in phase envelope.</td>
</tr>
<tr>
<td><strong>Quality Lines</strong></td>
<td>Lines of constant volumetric or molar percentage of a phase.</td>
</tr>
</tbody>
</table>
**Tx-diagram example:**
Cooling C₂/C₃ at a constant pressure of 5 barₜ

**Mixed-fluid process in Th-coordinates**
(50/50 w-% C₂/C₃)
Process licensors – Base load LNG plants

- Air Products and Chemicals Inc (APCI)
  - World leader since the 1970s – More than 130 Mtpa installed, 50 Mtpa under construction, more than 60 operating trains
  - C3MR process (< 60 trains)
  - AP-X™ Hybrid (Qatar Gas II, 2 x 7.8 Mtpa, Start up 2008 and 2009)
- ConocoPhillips (Optimised) Cascade
  - Trinidad: Atlantic LNG - 4 trains
  - Egypt: Idku
  - Alaska: Kenai (Operating since 1969!)
  - Australia: Darwin LNG
  - Equatorial Guinea
- Shell DMR – Double Mixed Refrigerant (Sakhalin, 2 x 4.8 Mtpa)
  - PMR (same as C3MR – but parallel MR circuits) – no references
- Linde/Statoil MFC® Mixed Fluid Cascade Process (Snøhvit, 4.3 Mtpa – start up 2007)
- Axens Liquefin™ (No references)

Mtpa = Million tonnes per year

Cascade process for natural gas liquefaction

[Diagram showing LNG liquefaction process with temperatures and pressures indicated]
Mixed-fluid process in Th-coordinates
(50/50 w-% C2/C3)

Principles of mixed refrigerant cycle
(Prico single-mix cycle)

<table>
<thead>
<tr>
<th>Composition:</th>
<th>NG</th>
<th>Refrig</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.897</td>
<td>0.360</td>
</tr>
<tr>
<td>C2</td>
<td>0.055</td>
<td>0.280</td>
</tr>
<tr>
<td>C3</td>
<td>0.018</td>
<td>0.110</td>
</tr>
<tr>
<td>nC4</td>
<td>0.001</td>
<td>0.150</td>
</tr>
<tr>
<td>N2</td>
<td>0.028</td>
<td>0.100</td>
</tr>
</tbody>
</table>
Mixed Fluid Cascade (MFC®) process (Linde-Statoil)

- Three mixed refrigerant circuits
  - Precooling (Mainly: C₂, C₃)
  - Liquefaction (Mainly: C₁, C₂, C₃)
  - Subcooling (Mainly: N₂, C₁, C₂)
- Cascade connection of the circuits
- Precooling in two (sometimes three) stages
- No fractionation of the mixed refrigerant flows
- Expander on subcooling cycle
Heavy hydrocarbon extraction
Scrubber column (Snøhvit)

- Natural gas liquids (NGL/LPG) are formed during precooling, and can/must be separated from the gas stream
- Propane and butane are valuable products
- Extraction process is needed to reach lean gas specifications, LNG specs demand that C₂ and C₃ is removed
- A relatively simple solution is to use a scrubber column that separates out liquid components which are formed during cooling of the natural gas
- Some LPG is fractionated to give pure C₁, C₂ and C₃ for refrigerant make-up
Natural gas circuiting

Composite temperature curves - Hammerfest

Overall Heat / Temperature Diagram for Cold Equipment in System 25
Sunbølt A Plant Feed Stock
Precooling circuit
VÆSKEDANNINGSKRETS

25-HX-101
25-HX-102
25-HA-114
25-KA-102
25-VD-105
25-HG-102
25-VD-104

FORKJØLINGSKRETS

25-HG-101
25-HG-102
25-HG-105
25-HG-104
25-VD-102
25-VD-103
25-VD-101
25-VD-103
25-VD-115
25-VG-110
25-VG-116
25-KA-101
27-HG-101

Classification: Internal
Status: Draft
Liquefaction technology – present and prediction
(Source: Shell)

Installed capacity to 2005
Newbuilt capacity 2006–2012 (estimate)
**Compressor driver alternatives**

- **Steam turbine**
  - Refrigerant compressor(s) driven by steam turbine
  - Common in older LNG plants
  - Steam plant needed, including boiler, feedwater treatment etc.

- **Gas turbine**
  - Direct mechanical compressor drive using gas turbine
  - Small plot area, low CAPEX
  - Most common solution today
  - Capacity of plant determined by available gas turbine sizes

- **Electric**
  - Only Snøhvit so far, but considered in several current developments
  - Increased availability, potential use of high-efficiency combined-cycle technology

**Compressor driver trends**

![LNG Refrigerant Compressor Drivers](chart.png)

- **Steam**
- **Frame 5**
- **Frame 6/7**
- **Electric**
- **Aerodervative**
Mixed Fluid Cascade (MFC) process and energy system at Hammerfest

Parallel drivers/compressors (increasing availability)

"Two in one" concept
Process availability (on-stream time)

<table>
<thead>
<tr>
<th>Circuit Configuration</th>
<th>Process Availability</th>
<th>On-line Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 circuits</td>
<td>GT 0.98 * GT 0.98</td>
<td>0.96</td>
</tr>
<tr>
<td>2 circuits + 1 parallel driver/compr</td>
<td>GT 0.98 * GT 0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>3 circuits</td>
<td>GT 0.98 * GT 0.98 * GT 0.98</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Heat rejection

Air cooling

Water cooling

Tube-in-shell heat exchanger
## Heat rejection

**Air cooling**
- Large plot area needed
- Lower process efficiency (less LNG for given power input)
- Lower CAPEX than water cooling
- Larger seasonal variation in capacity and efficiency

**Water cooling**
- More compact plant
- Costly corrosion-resistant materials needed (e.g. titanium)
- High process efficiency
- May need chlorination to prevent fouling

---

**Air cooled condensers**

![Image of air cooled condensers](image-url)
Cooling of LNG plants

Refrigerant Cooling Media Trends

<table>
<thead>
<tr>
<th>Year</th>
<th>Seawater</th>
<th>Freshwater</th>
<th>Air</th>
<th>Hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960</td>
<td>10%</td>
<td>35%</td>
<td>55%</td>
<td>4%</td>
</tr>
<tr>
<td>1970</td>
<td>10%</td>
<td>35%</td>
<td>55%</td>
<td>4%</td>
</tr>
<tr>
<td>1980</td>
<td>37%</td>
<td>10%</td>
<td>52%</td>
<td>4%</td>
</tr>
<tr>
<td>1990</td>
<td>37%</td>
<td>10%</td>
<td>52%</td>
<td>4%</td>
</tr>
<tr>
<td>2003</td>
<td>52%</td>
<td>7%</td>
<td>4%</td>
<td>4%</td>
</tr>
</tbody>
</table>